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(54) Series planar construction for solid electrolyte oxygen pump

Flachaufbau in Serien für Sauerstoffpumpe mit festem Elektrolyt

Série d'éléments constructifs plats pour pompe à oxygène à électrolyte solide

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Description

FIELD OF THE INVENTION

[0001] This invention relates to solid-state electrochemical deviceS capable of transporting ions through an electrolyte. Specifically, this invention relates to an apparatus for transporting ions through series planar structures which demonstrate improved electrical and pneumatic integrity.

BACKGROUND OF THE INVENTION

[0002] Conductive solids which transport ions, such as oxygen ions, are known in the art and are useful in many applications, including fuel cells, processes for producing, separating and purifying gases and gas sensing or monitoring. In certain applications, a series of electrolytic cells joined together provide increased electrochemical operation. An example of a series tubular system used as a fuel cell is disclosed in U.S. Patent No. 4,431,715.

[0003] Efficient operation of series tubular or planar cells has been compromised in prior art systems by inherent weaknesses in system design and configuration. For example, individual electrolytic cells are commonly joined together by means generally known as an interconnect, which seals the cells together and provides an electrical connection between the cells. Such interconnects often fail over time as the seals degrade at elevated operating temperatures due to corrosion between the electrical conductor and the seal of the interconnect.

[0004] Effective seals are difficult to form between the components making up these devices. For example, when silver or silver alloy based electrodes are employed, the maximum temperature of the sealing material must be limited to the melting temperature of silver or silver alloy. Moreover, when glass is used as a sealing material, sufficient viscosity under operating temperature must be maintained in order to retain a seal over sustained periods of time. Further problems have been experienced in prior art cells which are connected in series due to limitations associated with manifolding the cells. Typical prior art interconnects often do not allow variation in configuration and manifolding of the electrolyte cells because of loss in pneumatic integrity experienced when operating such systems.

[0005] A solid electrolyte oxygen pump is presented in U.S. Patent 4,877,506 which possesses electrodes which are shaped to form a plurality of linear, parallel channels on facing surfaces of the electrolyte. The air feed is directed into the channels formed of the air electrode and oxygen formed during operation of the device is removed by passage through the electrolyte via channels formed of the oxygen electrode or anode. A monolithic array is formed by stacking the cells with an interconnecting material between adjacent cells.

[0006] U.S. Patent 4,490,445 discloses a solid oxide electrochemical energy converter which comprises alternating layers of solid oxide electrolyte plates and electrical conductor plates. Each electrolyte plate includes a coating of a porous oxidizer electrode on a first surface of the electrolyte and a coating of a porous fuel electrode on a second surface of said the electrolyte. Each conductor plate includes groove networks formed by ridges which define gas passages on both surfaces of the conductor plate, such ridges being in electrical contact with the electrode coatings on next adjacent electrolytes. Each conductor plate also possesses a means for tapping electricity from or introducing electricity into the converter. The conductor plates also possess circumferential ridges arranged along the edges of the conductor plate to define gas seals, the ridges being in contact with surface coatings on next adjacent electrolyte plates which surface coatings possess the same composition as that of the electrode coatings.

[0007] U.S. Patent 5,217,822 discloses a solid oxide electrolyte fuel cell comprising a a solid electrolyte element composed of zirconia stabilized with yttria, a porous anode plate essentially composed of nickel and zirconia partly stabilized with magnesia, the anode plate having an integral portion serving as an anode, a porous cathode composed of lanthanum strontium manganite, a porous cathode plate composed of lanthanum strontium manganite and a separator composed of lanthanum chromite. The solid oxide electrolyte element, the cathode, the cathode plate and the separator are laminated on the anode plate in the enumerated order. The anode plate has formed on its surface opposite to the surface which contacts the solid electrolyte elements, a plurality of grooves in which a fuel gas flows. The cathode plate is also formed with a plurality of grooves in which an oxidizer gas flows on its surface facing the solid electrolyte element. After flowing in the grooves, the reaction gases pass through cavities in the electrode plates and are supplied to the solid electrolyte element.

[0008] EP-A-572 018 discloses a planar solid oxide fuel cell arrangement.

[0009] Electrochemical systems having improved interconnects between the cells to assure electrical and pneumatic integrity of the system are desired in order to provide sealing integrity between the cells and to provide a series planar electrolytic cell system having simplified interconnection of the cells while permitting variation in manifolding and configuration.

SUMMARY OF THE INVENTION

[0010] In accordance with the present invention, the solid state electrochemical structure for transporting ions includes a plurality of planar electrolytic cells joined together in series with electrical conductor means configured to provide electrical interconnection between each tubular or planar electrolytic cell, and further includes sealing means for securing each electrical conductor to each contiguous tubular or planar cell with

which each is associated to provide a pneumatic seal while permitting variation in manifolding and process configuration. Particular advantages are achieved when the planar cells are manifolded in a cross-flow configuration.

[0011] The electrochemical devices of the present invention can be used for a variety of processes including the separating of any ionizable component from a feedstream wherein such ionizable component is capable of being transported through the ionic conducting electrolyte layer. For example, the ionizable component may be oxygen present in air wherein oxygen ions are passed through the ionic conducting separation components comprising the electrochemical device. Hydrogen can also be separated from a feed stream by fabricating the ionic conducting electrolyte layer from a ceramic which is capable of transporting the ionized hydrogen species. These devices can also be readily adapted to function as partial oxidation devices wherein an oxygen-containing feedstream is introduced into one set of gas passages situated in the interconnecting layer of the device and a feedstock to be oxidized is introduced into the other set of gas passages whereby oxygen transported through the electrolyte layers is contacted with the feedstock to be oxidized.

[0012] Thus, the invention, as claimed, utilizes a first electrode and a second electrode. In the case wherein the ionic conducting electrolyte is chosen to conduct a negative ionic species such as in the case of separating oxygen from a oxygen-containing feedstream, the first electrode layer is the anode and the second electrode layer is the cathode. In the case wherein the ionic conducting electrolyte is chosen to conduct a positively charged ionic species such as in the case of separating hydrogen from a hydrogen-containing feedstream, the first electrode layer is the cathode and the second electrode layer is the anode.

[0013] The electrochemical devices can be formed from a series of planar cells which are generally flat bodies having opposing surfaces, for convenience referred to as a first surface and a second surface. Each flat plate may have a thickness ranging from 10 µm to about 1 cm. A preferred thickness is from about 20 µm to about 1 mm. The electrolyte is non-porous in order to prevent escape of gas from within the cell. The flat electrolytic cells are adapted with structural elements to receive gases therein, and each cell possesses one or more openings to provide communication between the cells when one or more stacks are manifolded.

[0014] Suitable electrolytes for making the planar cells include oxygen ion conducting ceramic metal oxides such as zirconia, ceria, hafnia, bismuth oxide and the like or mixtures containing such oxides when oxygen ion transport is desired. Electrolytes of this type are disclosed in U.S. Patent Nos. 4,725,346; 4,879,016; and 5,021,137. The ceramic used in the electrolytes may be doped with other materials, such as calcia, yttria or strontia. Electrolytes such as beta alumina, NASICON and the like may be used if sodium ion transport is desired.

[0015] An anode is associated with one surface of the flat plate, either the first surface or the second surface, while a cathode is associated with the opposing surface. In a particularly suitable planar cell, the anode is in the form of a coating adhered to the first surface of the plate and the cathode is in the form of a coating adhered to the second surface. Each planar cell of a multi-cell structure has the anode thereof associated with the same surface as every other planar cell.

[0016] The anode and cathode are porous or permeable to gas molecules thereby allowing gas to penetrate the electrode. Materials which are particularly suitable for use as electrodes (i.e. the cathode and anode) include silver, alloys of silver, composites of silver or silver alloys with one or more oxide ion-conductive materials. Such alloys preferably contain at least 50% silver. Metals which may be alloyed with silver or used instead of silver include palladium, platinum, gold and copper. In addition, some mixed conducting ceramic oxides may be used alone or in the form of composites with silver, including lanthanum strontium cobaltite, which is known to be particularly effective as an electrode for oxygen generation systems.

[0017] The anodic and cathodic materials may be applied to the respective surfaces of each planar cell by means known in the art. Such application methods include sintering of a paste material applied by screen printing or conventional coating techniques, plasma spraying or sputtering. The coating of electrode material on the electrolyte is substantially continuous, i.e. there are no spaces or breaks in the coating. The placement of the anode on one surface of the electrolyte is preferably coextensive with placement of the cathode on the opposing surface. The thickness of the anode or cathode on the ceramic electrolyte is generally between about 0.1 microns and about 100 microns, and preferably between about 1 to about 20 microns. The electrode layers are preferably thin in order to allow movement of gases freely therethrough. When very thin electrodes are used it may be desirable to use a current conductor, such as a metallic grid or a composite of the electrode with a silver coating applied over the electrode to minimize sheet resistance. From an ion transport standpoint, very thin electrolytes are preferred so long as the electrolyte possesses sufficient structural integrity. From a structural standpoint, thicker electrolytes may be required, especially if there is, or could be, a significant pressure differential across the electrolyte.

[0018] Planar cells can be connected in series by stacking wherein the substantially flat cells are likewise connected electrically by such interconnects. Likewise, aligning several planar cells in a stack arrangement is more advantageous than employing a single long planar cell because sheet resistance is reduced accordingly.

[0019] The interconnects of the tubular and planar systems are configured to form an electrical connection

between the anode of one cell and the cathode of an adjacent cell. The interconnects are formed of highly electrically conductive, substantially non-ionically conductive non-porous material which is preferably resistant to oxidation. The material used for the interconnects must also have a thermal expansion coefficient compatible with that of the material used to form the tubular or planar cells. Thus, when the tubular or planar cells expand under high temperature, the interconnects will similarly expand without damaging the individual cells or interconnects.

[0020] Examples of materials which may be used to form the interconnects include electrically conducting oxides like LSM (lanthanum strontium manganite), LSCr (lanthanum strontium chromite), LCM (lanthanum calcium manganite) and similar materials, and high chrome metal alloys such as Inconel® (600 series) (76% Ni, 15.5% Cr, 8% Fe) or stainless steel (400 series) and similar corrosion resistant metals. A particularly suitable material for the interconnect is $La_xSr_{1-x}MnO_3$ wherein x ranges from 0.2 to 0.7.

[0021] The interconnects are joined to the tubular or planar cells by sealing means which provide a gas-tight seal thereby preventing leakage of oxygen or other gases from within the tubular cells or between contiguous planar cells. Sealing means are formed between the electrolyte and the interconnect in a manner which provides a separation between the electrical pathway and the sealing means. Separation of the sealing means from the electrical pathway, in addition to the configuration of the interconnect, prevents deterioration of the seal resulting from high temperature operation of the electrochemical device.

[0022] The sealing means comprises a sealant material which provides a comprehensive, gas-tight barrier between specified components. For tubular cells, the sealing means provides a gas tight barrier between the feed and product gases and is situated between an end surface of the interconnect and the adjacent end surface of an electrolytic cell. For planar cells, the sealant is a gas tight barrier situated between two surfaces of an interconnect and adjacent cells in which case a comprehensive, gastight barrier is provided between the feed gas, product gas and the external environment.

[0023] The sealant material must also have a thermal expansion coefficient comparable to that of the interconnect material and the electrolyte. A particularly suitable sealant is a devitrifying glass, i.e. a glass material which, after being melted and thermally treated, converts to a glass/ceramic upon cooling. An example of a suitable devitrifying glass is a lithium alumino-silicate. Other examples of suitable sealants include glass, glass-ceramic composites, glass-metal composites, oxidation resistant metal alloys, brazes such as Ag/Pd alloys and the like.

[0024] In a first embodiment of the planar system, an electrically conducting interconnect layer having gas passages formed on its surfaces is positioned between two planar electrolytic cells. Communicating layers of conductive material join the anode layer of one cell to the first surface of the interconnect layer, and join the second surface of the interconnect layer to the cathode layer of an adjacent cell thereby forming an electron path between the electrodes via the electrically conducting interconnect layer. Sealant is placed relative to the interconnect layers and the planar cells in a manner which forms a seal therebetween but is remote from the electrical pathway of the interconnect layer. The conductive material positioned between the electrode layers and the interconnect layer may be a conductive metal such as silver, a silver alloy, platinum, a paste of the electrode or interconnect materials, and the like.

[0025] The planar system can be configured to allow for a variety of manifolding or stacking arrangements while maintaining electrical and pneumatic integrity of the system. End plates and coupling structure are provided which, when placed at the end of a series of planar cells, permits stacking, or aggregation, of numerous planar cells. There is provided a positive end plate which forms an electrical connection with the anode of a terminal planar cell, and a negative end plate which forms an electrical connection with the cathode of a terminal planar cell. The end plates are made from electrically conductive materials as described previously in connection with the interconnect layers and may have gas passages on the surfaces adjacent to the electrode layers. The end plates are formed to the ends of the planar cells as described with respect to the interconnect layers and sealing means are positioned to provide a pneumatic seal.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] In the drawings, which illustrate what is currently considered to be the best mode for carrying out the invention,

FIG. 1 illustrates an electrochemical structure comprising a first planar cell and a second planar cell which are joined in series by an interconnect positioned between such first planar cell and the second planar cell;

FIG. 2 further illustrates the electrochemical structure according to FIG. 11 wherein the cells are manifolded to capture product formed during operation.

FIG. 3 illustrates an alternative embodiment for separating oxygen from air which employs a plurality of stacks connected pneumatically in parallel via collection manifolds.

DETAILED DESCRIPTION OF THE INVENTION

[0027] FIG. 1 presents an embodiment of the present invention wherein a plurality of planar solid electrolyte

cells are integrated in a series configuration. As shown in FIG. 1, the electrochemical structure 310 of the invention includes a plurality of electrolytic cells 312, 314 joined together by an electrically conducting interconnect layer 316. Interconnect layer 317 would likewise to used to join electrolytic cell 314 and another electrolytic cell or would form the terminus of the device via an end cap (not shown). The electrolytic cells 312, 314 consist of ion conducting electrolyte layers 318 and 320 having a first surface and a second surface. The ion conducting electrolyte layers 318, 320 of the electrolytic cell 312, 314 are about 5 μm to 1 mm thick.

[0028] The electrolyte layers 318, 320 may be formed of materials such as zirconia, hafnia, bismuth oxide, ceria used in the tubular design embodiment and are preferably formed from a multicomponent ionic conducting metallic oxide comprising an oxide of at least two different metals or a mixture of at least two different metal oxides wherein the multicomponent metallic oxide demonstrates ionic conductivity at device operating temperatures, typically greater than about 500°C. Such ionically conducting multicomponent metallic oxides are represented by the formula $A_xA'_{x'}A''_{x''}O_z$, where A,A',A" may be independently selected from Groups 2, 3, 13, 14 and 15, the F block lanthanides and the D block transition metals according to the Periodic Table of the Elements adopted by the IUPAC wherein $0<x\leq1$, $0<x'\leq1$, $0\leq x''\leq1$, $x+x'+x''=1$ and z is a number which renders the compound charge neutral. A representative example is $Y_{0.182}Zr_{0.818}O_{1.909}$ which has an oxygen ionic conductivity of 0.1 $ohm^{-1}cm^{-1}$ at 1000°C and an ionic transport number (the ratio of the ionic conductivity to the total conductivity) of close to 1. Other examples include $Sr_{0.1}Ce_{0.9}O_{1.9}$ and $Bi_{0.875}V_{0.125}O_{0.687}$.

[0029] Anode layers 326, 328 are formed to the first surface of the electrolyte layers 318, 320 of the cells 312, 314. The anode layers 326, 328 can be formed from an oxidation-resistant metal, an alloy or a multicomponent mixed conducting oxide represented by the formula $A_xA'_{x'}A''_{x''}B_yB'_{y'}B''_{y''}O_{3-z}$, where A,A',A" are chosen from the group comprising Groups 1, 2 and 3 and the F block lanthanides; and B,B',B" are chosen from the D block transition metals according to the Periodic Table of the Elements adopted by the IUPAC wherein $0<x\leq1$, $0\leq x'\leq1$, $0\leq x''\leq1$, $0<y\leq1$, $0\leq y'\leq1$, $0\leq y''\leq1$, $x+x'+x''=1$, $y+y'+y''=1$ and z is a number which renders the compound charge neutral, or a metal (or alloy) or a mixture of the two. For example the anode layers 326, 328 can be formed from $La_xSr_{1-x}CoO_{3-z}$ wherein x ranges from 0.2 to 1.0 and z is a number which renders the compound charge neutral (lanthanum strontium cobaltite or LSCO) with an intermediate coating of lanthanum strontium cobaltite and silver or silver-palladium alloy is applied to the first surface of the electrolyte 318, 320. The coating can be attached by sintering of a paste, applied, for example, by screen printing or by sputtering, or other techniques well known in the art. The thickness of the anode 326, 328 is about 0.1 to 100 microns.

[0030] Cathode layers 330, 332 are formed to the second surface of electrolyte layers 318, 320 of the cells 312, 314. Cathode layers 330, 332 may comprise a coating of an oxidation-resistant metal, an alloy or a multicomponent mixed conducting oxide according to the previously described formula For example, LSCO may be placed on the electrolyte with an intermediate coating thereover of LSCO-silver alloy, such alloy having at least 50% silver as a component thereof. Cathode layers 330, 332 are formed to the second surface of electrolyte layers 318, 320 in a manner similar to that of anode layers 326, 328. The thickness of the cathode material is about 0.1 to 100 microns. The coating of anode layers 326, 328 on the first surface of electrolyte layers 318, 320 is coextensive with the coating of cathode layers 330, 332 on the second surface of the electrolyte layer.

[0031] Particularly suitable materials for fabricating the anode layer and cathode layer of this planar embodiment include lanthanum strontium cobaltite, lanthanum strontium cobalt ferrite, lanthanum barium cobaltite, strontium cobalt ferrite and lanthanum barium cobalt ferrite. Alternately, the cathode and anode layers may additionally contain silver or an alloy of silver.

[0032] Adjacent electrolytic cells 312, 314 are joined together by an interconnect layer 316. The interconnect layer 316 is made of an oxidation resistant material having a thermal expansion coefficient comparable to electrolyte layers 318, 320, a high electronic conductivity and low ionic conductivity. The material can be a multicomponent, electronically conducting oxide of the composition previously described, a metal or alloy, or a mixture of the two. Suitable electronically conducting oxides include lanthanum strontium manganite, lanthanum strontium chromite, lanthanum calcium manganite and lanthanum calcium chromite. Channels are formed, e.g., by pressing or layering tapes, in the second surfaces of the interconnects. Gas passages 322, 324 are formed between the first surface of the interconnect and the adjacent anode 326, 328, and serve to collect the product oxygen. Gas passages 300, 302 are formed between the second surface of the interconnect layer and the adjacent cathode layer 332 and serve to introduce the feed oxygen-containing gas to the device.

[0033] The respective gas passages for introducing the feed gas into the device and the gas passages for collecting the oxygen product or other gaseous product can be configured in a fashion to accommodate the manifolding desired for a particular application. Preferably, the respective gas passages are configured such that the passages for introducing the oxygen-containing gas run in a direction substantially perpendicular to the gas passages employed to collect the oxygen produced in the device. Thus, manifolds can be conveniently attached to one, two or more cells. Alternately, the respective gas passages are configured such that the passages for introducing oxygen-containing gas run in a direct substantially parallel to the gas passages employed to collect the oxygen product thereby allowing co-current

or counter-current flow schemes. Of course, the orientation of the respective gas passages can be varied between such extremes.

[0034] As illustrated by FIG. 1, the first surface of the interconnect layer 316 is adjacent the anode layer 326 of cell 312. A conductive material 340, 341 such as silver or silver alloy or the material of the anode layer or interconnect layer, may optionally be formed between the anode layer 326 and the interconnect layer 316 and anode layer 328 and the interconnect layer 317. Similarly, the second surface (not shown) of the interconnect layer 316 is adjacent the cathode layer 332 of cell 314, and a conductive material 342 may optionally be formed between the interconnect layer 316 and the cathode layer 332. The conductive material 340, 342 serves to direct electrons from the anode layer 326 to the interconnect layer 316, and from the interconnect layer 316 to the cathode layer 332.

[0035] To effect a gas-tight seal between the cells 312, 314 and the interconnect layer 316, sealing means in the form of a sealant are positioned therebetween. That is, a sealant 348 of a suitable composition such as devitrifying glass is formed between the interconnect layer 316 and two opposite edges of the second surface of the electrolyte 320 by placement of a bead of glass material thereabout. The bead is then heated to melt the material. The devitrifying glass material has a melting point less than that of any other component of the cell and heating of the sealant to form the seal does not affect the electrode material. Upon cooling, the devitrifying glass turns to a glass/ceramic. Similar beads of devitrifying glass sealant 349, 350 are positioned between opposite edges of the first surface of the adjacent electrolyte layers 318, 320 and the interconnect layers 316, 317 and are heated and cooled to form a gas-tight seal. Alternatively, the seals 348, 349 and 350 can be composed of a suitable oxidation resistant metal braze alloy such as Ag/Pd. It is notable that the sealant 348 on the second surface of the interconnect 316 is positioned so that it is separated from the electron pathway of the interconnect layer 316. Likewise, the sealant 350 on the first surface of the interconnect layer 317 is separated from the electron pathway of interconnect layer 317.

[0036] Planar electrochemical cells can be produced by the following general procedure wherein the material for the cathode layer, anode layer, interconnect layer and electrolyte layer are chosen from any of the previously enumerated materials. Initially, a coating of conducting material such as LSCO is applied to both the first and second surfaces of the desired electrolyte layer. The cells are then fired at a temperature ranging from 1050 to about 1200°C. An intermediate coating of a mixture of LSCO and silver/palladium alloy is then placed on the LSCO coatings of the surfaces of each cell. A particularly suitable composition for the intermediate coating is about 75% LSCO to about 25% silver-palladium alloy. The ratio of silver to palladium in the alloy may vary, but a ratio of 70% to 30% is suitable. The intermediate coating is fired to both surfaces of the cells at a temperature ranging from 1050 to about 1200°C. Alternately, both coatings may be fired simultaneously. The cells are then joined face-to-face and in electrical series by attachment of the interconnect layers. The interconnect layers are attached to the cells by application of the devitrifying glass which may be screen printed as a paste onto either the electrolyte plates or interconnects before assembly of the stack The stacks are fired at a temperature ranging from 900 to about 1100°C.

[0037] In operation, an electrical voltage is applied across the end member interconnect layer at the top and bottom of the stack. The end member interconnect layer may have only one set of channels formed in their surfaces adjacent to the electrode layers. Electrons flow from the anode layer on the first surface of an electrolyte layer through the pathway of the interconnect layer to the cathode layer of the adjacent cell. When the series stacked planar system is used, for example, in the production or enrichment of oxygen gas, a feed stream such as air or a process off-gas is passed through the gas passages 300, 302. Electrons at the cathode layer ionize oxygen molecules to oxygen ions. The oxygen ions pass through the electrolyte layer via the influence of an applied voltage differential to the anode layer where the electrons are given up and oxygen molecules are formed inside the gas passages 322, 324. The electrons given up at the anode layer continue to travel through the interconnect layer to the cathode layer of an adjacent cell where the process continues at that cell.

[0038] The dimension of the gas passages formed in the interconnect layer may be optimized for specific functions and operating conditions of the stack of planar cells. For example, in a deoxygenating application when the feed gas contains <5% O_2 and the objective is to remove oxygen from the stream to a level of < 1 ppm, the depth of the gas passages 300, 302 may be reduced to minimize the diffusion path length of oxygen to the cathode surface. In this instance, the depth can be < 1 mm, while the width and spacing of the passages are set by considerations of pressure drop through the gas passages, the electrical sheet resistance of the cathode and the mechanical strength of the cell assembly. The gas passages may contain additional ribs, static mixers and other features to minimize gas phase diffusion resistance.

[0039] The gas passages may be fabricated within the interconnect layer in a wide variety of shapes, in cross-section, such as rectangular, trapezoidal, semi-circular and the like. The depth and spacing of the passages may be widely varied and optimum designs may be assessed for a given application without undue experimentation. For example, the depth of a passage may decrease with distance traversed across the surface of the electrode layer in order to increase the diffusional flux to the electrode surface of the component gas being transported through the electrolyte. In an alternate embodiment, (not illustrated) the individual gas passages

shown in FIG. 11 may be partially or totally replaced by means for minimizing gas phase diffusion resistance. A suitable means comprises a repeating network of isolated cylindrical, conical or rectangular pins, designed to distribute gas flow while minimizing pressure drop during operation.

[0040] A plurality of planar electrolytic cells can be joined in series to another plurality of planar cells to provide an integrated system of interconnected electrolytic cells as depicted in FIG. 2. Oxygen-containing gas feed may be introduced into the gas passages 400 via feed inlet 408 of manifold 401 and oxygen depleted gas is then withdrawn from the feed outlet 410 of manifold 402. The separated oxygen exuding from the gas passages 422 may be collected by manifolds 404, 406 attached to faces of the stack perpendicular to the manifolds 401, 402 and exits via outlets 412 and 414. The manifolds are sealed to the faces of the stacks to prevent short-circuitry of adjacent cells, for example, with an electrically insulating devitrifying or glassy sealant.

[0041] A direct current or rectified alternating current power supply 421 is connected across the end-member interconnects 416 and 418. When oxygen is being transported through the electrolyte, the negative terminal of the power supply is connected to the end cathode interconnect layer 416 (via an optional end plate or coating 417) and the positive terminal is connected to the end anode interconnect layer 418 (also via optional end plate or coating 419). A sufficient voltage is applied across the stacks to drive current through the stacks causing the oxygen separation process to occur.

[0042] In an alternative embodiment, for example, to separate oxygen from air, a plurality of stacks 506 may be connected pneumatically in parallel via their oxygen collection manifolds 500, 502 as illustrated in FIG. 3. The stacks may be mounted in a common air feed plenum 504, further equipped with a gas distributor plate 510, the spaces between the individual stacks being filled with an inert insulation (not shown). Electrical connection between stacks may be either in series or parallel configurations, or a combination thereof as is conventional in the art.

[0043] When the electrochemical device is operated to remove oxygen from an oxygen-containing gaseous mixture, such mixture is introduced into the stacks in parallel via manifold 500 and an oxygen depleted gaseous mixture is collected via manifolds 502. The oxygen removed during operation of the device is collected via plenum 504. Alternately, the manifolds may be configured such that the oxygen-containing gaseous mixtures passes through alternating stacks in a series flow configuration.

[0044] The electrochemical device of the present invention provides an interconnected series of planar electrolytic cells which maintains electrical and pneumatic integrity during operation. The configuration of the interconnect and the placement of sealant provides a gastight barrier between the internal and external environments of the electrolytic cells while avoiding deterioration or corrosion of the seal due to high operating temperatures.

Claims

1. An electrochemical solid-state device for transporting ions through an electrolyte comprising: a plurality of solid oxide planar electrolytic cells (312, 314), each electrolytic cell comprising an ion conducting electrolyte layer (318, 320), a first electrode layer situated contiguous to a first surface of the electrolyte layer and a second electrode layer situated contiguous to a second surface of the electrolyte layer, and an electrically conductive interconnect layer (316) being disposed in a face-to-face arrangement between the plurality of planar cells and providing a pathway for movement of electrons between the first electrode layer of the second planar electrolytic cell and the second electrode layer of the first planar electrolytic cell, <u>characterised in that</u> the solid oxide planar electrolytic cells (312, 314) are contiguously stacked in series by the electrically conductive interconnect layer (316) and by a sealing means (348) to form a gas-tight seal therebetween and in that, on the first surface, the interconnect layer forms at least one gas passage (322, 324) between the surface of the interconnect layer and the adjacent electrode layer (332) for receiving a feedstream containing a component capable of being transported ionically through the electrolyte, which first surface of the interconnect layer is connected to the second electrode layer of a first planar electrolytic cell (312), and in that a second surface of the interconnect layer is connected to the first electrode layer of a second planar electrolytic cell (314), wherein, on the second surface channels are formed by pressing or layering tapes and the interconnect layer forms at least one gas passage (300, 302) between the surface of the interconnect layer and the adjacent electrode layer (322, 324) for withdrawing the component being transferred through the electrolyte layer.

2. The electrochemical device according to Claim 1 where the gas passage on the first surface of the electrically conductive interconnect layer of each respective electrolytic cell are aligned substantially perpendicular to the gas passage on the second surface of the electrically conductive interconnect layer.

3. The electrochemical device according to Claim 2 wherein the gas passage on the first and second surfaces of the interconnect layer of each respective electrolytic cell further comprise a means for reducing gas phase diffusion resistance.

4. The electrochemical device according to Claim 3 wherein the means for minimizing gas phase diffusion resistance comprises pins, ribs or static mixers.

5. The electrochemical device according to Claim 1 wherein the ion conducting electrolyte layer of each planar electrolytic cell is independently selected from a multicomponent ionic conducting metallic oxide comprising an oxide of at least two different metals or a mixture of at least two different metal oxides.

6. The electrochemical device according to Claim 5 wherein the multicomponent ionic conducting metallic oxide is represented by the formula $A_xA'_{x'}A''_{x''}O_z$, where A,A',A" may be independently selected from Groups 2, 3, 13, 14, and 15, the F block lanthanides and the D block transition metals according to the Periodic Table of the Elements adopted by the IUPAC wherein $0<x\leq1$, $0<x'\leq1$, $0\leq x''\leq1$, $x+x'+x''=1$ and z is a number which renders the compound charge neutral.

7. The electrochemical device according to Claim 6 wherein the multicomponent ionic conducting metallic oxide is selected from the group consisting of calcia-doped ceria, yttria-doped ceria, strontia-doped ceria, yttria-magnesia-doped zirconia, yttria-doped zirconia, bismuth-vanadium oxide, ceria and hafnia.

8. The electrochemical device according to Claim 2 wherein the anode layer and the cathode layer of each respective planar electrolytic cell independently comprise a multicomponent mixed conducting oxide.

9. The electrochemical device according to Claim 8 wherein the multicomponent mixed conducting oxide is represented by the formula $A_xA'_{x'}A''_{x''}B_yB'_{y'}B''_{y''}O_z$, where A,A',A" are chosen from the group comprising Groups 1, 2 and 3 and the F block lanthanides; and B,B',B" are chosen from the D block transition metals according to the Periodic Table of the Elements adopted by the IUPAC wherein $0<x\leq1$, $0\leq x'\leq1$, $0\leq x''\leq1$, $0<y'\leq1$, $0\leq y'\leq1$, $0\leq y''\leq1$, $x+x'+x''= 1$, $y+y'+y''=1$ and z is a number which renders the compound charge neutral.

10. The electrochemical device according to Claim 9 wherein the multicomponent mixed conducting oxide is selected from the group consisting of lanthanum strontium cobaltite, lanthanum strontium cobalt ferrite, lanthanum barium cobaltite, lanthanum barium cobalt ferrite and strontium cobalt ferrite.

11. The electrochemical device according to Claim 1 wherein the anode layer and the cathode layer of each respective planar electrolytic cell independently comprise a metal or alloy.

12. The electrochemical device according to Claim 11 wherein the anode layer and the cathode layer of each respective planar electrolytic cell contain silver.

13. The electrochemical device according to claim 1 wherein the electrically conductive interconnect layer comprises an oxidation-resistant metal or an alloy

14. The electrochemical device according to Claim 1 wherein the electrically conductive interconnect layer of each respective planar electrolytic cell comprises a multicomponent electronically conductive metallic oxide.

15. The electrochemical device according to Claim 14 wherein the multicomponent electronically conductive metallic oxide is selected from the group consisting of lanthanum strontium manganite, lanthanum strontium chromite and lanthanum calcium manganite and lanthanum calcium chromite.

16. The electrochemical device according to Claim 2 wherein the sealing means maintains a gas-tight seal at temperatures greater than 500°C and has a thermal expansion coefficient comparable to that of the electrically conductive interconnect layer and ion conducting electrolyte layer.

17. The electrochemical device according to Claim 16 wherein the sealing means is selected from the group consisting of devitrifying glass, glass, glass-ceramic composites, glass-metal composites, and oxidation resistant metal alloys and brazes.

Patentansprüche

1. Elektrochemische Vorrichtung im festen Zustand zum Transportieren von Ionen durch einen Elektrolyten mit: Mehreren planaren bzw. flachen Festoxid-Elektrolytzellen (312, 314), wobei jede Elektrolytzelle umfaßt: eine ionenleitende Elektrolytschicht (318, 320), eine erste Elektrodenschicht, die im Anschluß an eine erste Oberfläche der Elektrolytschicht angeordnet ist, und eine zweite Elektrodenschicht, die angrenzend an eine zweite Oberfläche der Elektrolytschicht angeordnet ist, und eine elektrisch leitende Zwischenverbindungsschicht (316), die in einer Fläche-an-Fläche-Anordnung zwischen der Vielzahl der planaren Zellen angeordnet ist und eine Bahn für die Bewegung von Elektronen zwischen der ersten Elektrodenschicht der zweiten

planaren Elektrolytzelle und der zweiten Elektrodenschicht der ersten planaren Elektrolytzelle bereitstellt, dadurch gekennzeichnet, daß die planaren Festoxid-Elektrolytzellen (312, 314) angrenzend in Serie bzw. Reihe mittels der elektrisch leitenden Zwischenverbindungsschicht (316) und mittels einer Versiegelungs- bzw. Dichtungseinrichtung (348) gestapelt sind, um eine gasdichte Versiegelung bzw. Abdichtung dazwischen auszubilden, und dadurch, daß die Zwischenverbindungsschicht an der ersten Oberfläche mindestens eine Gaspassage (322, 324) zwischen der Oberfläche der Zwischenverbindungsschicht und der benachbarten Elektrodenschicht (332) zum Aufnehmen einer Einspeisungsströmung ausbildet, die eine Komponente enthält, die ionisch durch den Elektrolyten transportiert werden kann, wobei die erste Oberfläche der Zwischenverbindungsschicht mit der zweiten Elektrolytschicht einer ersten planaren Elektrolytzelle (312) verbunden ist, und dadurch, daß eine zweite Oberfläche der Zwischenverbindungsschicht mit der ersten Elektrodenschicht einer zweiten planaren Elektrolytzelle (314) verbunden ist, wobei auf der zweiten Oberfläche Kanäle durch Pressen oder durch Streifenschichtung ausgebildet werden, und die Zwischenverbindungsschicht mindestens eine Gaspassage (300, 302) zwischen der Oberfläche der Zwischenverbindungsschicht und der angrenzenden Elektrodenschicht (322, 324) ausbildet, um die Komponente abzuziehen, die durch die Elektrolytschicht hindurchtransportiert wird.

2. Elektrochemische Vorrichtung nach Anspruch 1, bei der die Gaspassagen auf der ersten Oberfläche der elektrisch leitenden Zwischenverbindungsschicht jeder jeweiligen Elektrolytzelle im wesentlichen senkrecht zu den Gaspassagen auf der zweiten Oberfläche der elektrisch leitenden Zwischenverbindungsschicht ausgerichtet sind.

3. Elektrochemische Vorrichtung nach Anspruch 2, bei der die Gaspassagen an den ersten und zweiten Oberflächen der Zwischenverbindungsschicht jeder Elektrolytzelle ferner eine Einrichtung zur Verringerung des Gasphasen-Diffusions-Widerstandes aufweisen.

4. Elektrochemische Vorrichtung gemäß Anspruch 3, bei der die Einrichtung zur Minimierung des Gasphasen-Diffusions-Widerstandes Stifte, Rippen oder statische Mischer umfaßt.

5. Elektrochemische Vorrichtung nach Anspruch 1, bei der die ionenleitende Elektrolytschicht jeder planaren bzw. flachen Elektrolytzelle unabhängig aus einem mehrkomponentigen ionisch leitenden Metalloxid ausgewählt wird, welches ein Oxid mindestens zweier Metalle oder ein Gemisch mindestens zweier verschiedenen Metalloxide umfaßt.

6. Elektrochemische Vorrichtung nach Anspruch 5, bei der das mehrkomponentige. ionisch leitende Metalloxid durch die Formel $A_xA'_{x'}A''_{x''}O_z$ repräsentiert wird, wobei A, A', A" unabhängig aus den Gruppen 2, 3, 13, 14 und 15, den F-Block-Lanthaniden und den D-Block-Übergangsmetallen gemäß dem Periodensystem der Elemente, das von der IUPAC verwendet wird, ausgewählt werden können, wobei $0 < x \leq 1$, $0 < x' \leq 1$, $0 \leq x'' \leq 1$, $x + x' + x'' = 1$ und z eine Zahl ist, welche die Verbindung ladungsneutral macht.

7. Elektrochemische Vorrichtung nach Anspruch 6, bei der das mehrkomponentige, ionisch leitende Metalloxid aus einer Gruppe ausgewählt wird, die besteht aus mit Calciumoxid (calcia) dotiertem Zeroxid (certa), mit Yttriumoxid (yttria) dotiertem Zeroxid (ceria), mit Strontiumoxid (strontia) dotiertem Zeroxid (ceria), mit Yttriumoxid(yttria)-Magnesiumoxid (magnesia) dotiertem Zirkonoxid (zirconia), mit Yttriumoxid (yttria) dotierem Zirkonoxid (zirconia), Bismuth-Vanadium-Oxid, Zeroxid (ceria) und Hafniumoxid (hafnia).

8. Elektrochemische Vorrichtung nach Anspruch 2, bei der die Anodenschicht und die Kathodenschicht jeder jeweiligen planaren bzw. flachen Elektrolytzelle unabhängig ein mehrkomponentiges leitendes Mischoxid aufweisen.

9. Elektrochemische Vorrichtung nach Anspruch 8, bei der das mehrkomponentige leitende Mischoxid durch die Formel $A_xA'_{x'}A''_{x''}B_yB'_{y'}B''_{y''}O_z$ repräsentiert wird, wobei A, A', A" aus der Gruppe ausgewählt wird, die die Gruppen 1, 2 und 3 und die F-Block-Lanthaniden umfaßt, und B, B', B" werden ausgewählt aus den D-Block-Übergangsmetallen, gemäß dem Periodensystem der Elemente, das von der IUPAC verwendet wird, wobei $0 < x \leq 1$, $0 \leq x' \leq 1$, $0 \leq x'' \leq 1$, $0 < y \leq 1$, $0 \leq y' \leq 1$, $0 \leq y'' \leq 1$, $x + x' + x'' = 1$, $y + y' + y'' = 1$ und z eine Zahl ist, welche die Verbindung ladungsneutral macht.

10. Elektrochemische Vorrichtung nach Anspruch 9, bei der das mehrkomponentige leitende Mischoxid aus der Gruppe ausgewählt wird, die Lanthan-Strontium-Kobaltit, Lanthan-Strontium-Kobalt-Ferrit, Lanthan-Barium-Kobaltit, Lanthan-Barium-Kobalt-Ferrit und Strontium-Kobalt-Ferrit besteht.

11. Elektrochemische Vorrichtung nach Anspruch 1, bei der die Anodenschicht und die Kathodenschicht jeder jeweiligen planaren Elektrolytzelle unabhängig ein Metall oder eine Legierung umfassen.

12. Elektrochemische Vorrichtung nach Anspruch 11, bei der die Anodenschicht und die Kathodenschicht jeder jeweiligen planaren Elektrolytzelle Silber enthalten.

13. Elektrochemische Vorrichtung nach Anspruch 1, bei der die elektrisch leitende Zwischenverbindungsschicht ein oxidationswiderstandsfähiges Metall oder eine Legierung umfaßt.

14. Elektrochemische Vorrichtung nach Anspruch 1, bei der die elektrisch leitende Zwischenverbindungsschicht jeder jeweiligen planaren Elektrolytzelle ein mehrkomponentiges elektronisch leitendes Metalloxid umfaßt.

15. Elektrochemische Vorrichtung nach Anspruch 14, bei der das mehrkomponentige, elektronisch leitende Metalloxid aus der Gruppe ausgewählt wird, die aus Lanthan-Strontium-Manganit, Lanthan-Strontium-Chromit, Lanthan-Calcium-Manganit und Lanthan-Calcium-Chromit besteht.

16. Elektrochemische Vorrichtung nach Anspruch 2, bei der die Versiegelungs- bzw. Dichtungseinrichtung eine gasdichte Versiegelung bzw. Dichtung bei Temperaturen aufrechterhält, die höher sind als 500°C, und einen Wärmeausdehnungskoeffizienten aufweist, der vergleichbar ist mit demjenigen der elektrisch leitenden Zwischenverbindungsschicht und der ionenleitenden Elektrolytschicht.

17. Elektrochemische Vorrichtung nach Anspruch 16, bei der die Versiegelungseinrichtung aus der Gruppe ausgewählt wird, die aus entglasendem Glas, Glas, GlasKeramik-Verbundwerkstoffen, Glas-Metall-Verbundwerkstoffen und oxydationswiderstandsfähigen Metallegierungen und Loten besteht.

Revendications

1. Dispositif électrochimique à l'état solide servant à transporter des ions à travers un électrolyte, comportant : plusieurs cellules électrolytiques planes (312, 314) à oxyde solide, chaque cellule électrolytique comportant une couche d'électrolyte (318, 320) ioniquement conductrice, une première couche d'électrode située en position contiguë à une première surface de la couche d'électrolyte et une deuxième couche d'électrolyte située en position contiguë à une deuxième surface de la couche d'électrolyte, et une couche d'interconnexion (316) électriquement conductrice disposée en agencement face à face entre les cellules planes et fournissant un parcours pour le déplacement d'électrons entre la première couche d'électrode de la deuxième cellule électrolytique plane et la deuxième couche d'électrode de la première cellule électrolytique plane, caractérisé en ce que les cellules électrolytiques planes (312, 314) à oxyde solide sont empilées en positions contiguës en série à l'aide de la couche d'interconnexion (316) électriquement conductrice et d'un moyen d'étanchéité (348), de manière à assurer entre elles un joint d'étanchéité aux gaz, et en ce que, sur la première surface, la couche d'interconnexion forme au moins un passage pour le gaz (322, 324) entre la surface de la couche d'interconnexion et la couche d'électrode (332) adjacente, pour recevoir un écoulement d'alimentation contenant un composant apte à être transporté ioniquement à travers l'électrolyte, laquelle première surface de la couche d'interconnexion est connectée à la deuxième couche d'électrode d'une première cellule électrolytique plane (312), et en ce qu'une deuxième surface de la couche d'interconnexion est connectée à la première couche d'électrode d'une deuxième cellule électrolytique plane (314), tandis que, sur la deuxième surface, des canaux sont formés en pressant ou en disposant des rubans en couche, la couche d'interconnexion formant au moins un passage pour le gaz (300, 302) entre la surface de la couche d'interconnexion et la couche d'électrode (322, 324) adjacente, pour extraire le composant transféré à travers la couche d'électrolyte.

2. Dispositif électrochimique selon la revendication 1, dans lequel le passage pour le gaz prévu sur la première surface de la couche d'interconnexion électriquement conductrice de chaque cellule électrolytique respective est aligné essentiellement à la perpendiculaire du passage pour le gaz prévu sur la deuxième surface de la couche d'interconnexion électriquement conductrice.

3. Dispositif électrochimique selon la revendication 2, dans lequel le passage pour le gaz prévu sur la première et sur la deuxième surface de la couche d'interconnexion de chaque cellule électrolytique respective comporte en outre un moyen pour réduire la résistance à la diffusion en phase gazeuse.

4. Dispositif électrochimique selon la revendication 3, dans lequel le moyen pour minimiser la résistance à la diffusion en phase gazeuse comporte des colonnettes, des nervures ou des mélangeurs statiques.

5. Dispositif électrochimique selon la revendication 1, dans lequel la couche d'électrolyte ioniquement conducteur de chaque cellule électrolytique plane est choisie indépendamment parmi un oxyde métallique ioniquement conducteur à plusieurs composants comportant un oxyde d'au moins deux mé-

taux différents ou un mélange d'au moins deux oxydes métalliques différents.

6. Dispositif électrochimique selon la revendication 5, dans lequel l'oxyde métallique ioniquement conducteur à plusieurs composants est représenté par la formule $A_xA'_{x'}A''_{x''}O_z$, dans laquelle A, A', A" peuvent être choisis indépendamment parmi les groupes 2, 3, 13, 14 et 15, les lanthanides du bloc F et les métaux de transition du bloc D du tableau périodique des éléments adopté par l'IUPAC, avec $0<x\leq1$, $0\leq x'\leq1$, $0\leq x''\leq1$, $x+x'+x''=1$, et z est un nombre qui annule la charge du composé.

7. Dispositif électrochimique selon la revendication 6, dans lequel l'oxyde métallique ioniquement conducteur à plusieurs composants est choisi dans l'ensemble constitué de l'oxyde de cérium dopé par l'oxyde de calcium, de l'oxyde de cérium dopé par l'yttria, de l'oxyde de cérium dopé par l'oxyde de strontium, de la zircone dopée par l'oxyde d'yttrium et la magnésie, de la zircone dopée par l'oxyde d'yttrium, de l'oxyde de bismuth et de vanadium, de l'oxyde de cérium et de l'oxyde d'hafnium.

8. Dispositif électrochimique selon la revendication 2, dans lequel la couche d'anode et la couche de cathode de chaque cellule électrolytique plane respective comportent indépendamment un oxyde conducteur mixte à plusieurs composants.

9. Dispositif électrochimique selon la revendication 8, dans lequel l'oxyde conducteur mixte à plusieurs composants est représenté par la formule $A_xA'_{x'}A''_{x''}B_yB'_{y'}B''_{y''}O_z$ dans laquelle A, A', A" sont choisis dans le groupe comprenant les groupes 1, 2 et 3 et les lanthanides du bloc F; et B, B', B" sont choisis parmi les métaux de transition du bloc D du tableau périodique des éléments adopté par l'IUPAC, avec $0<x\leq1$, $0\leq x'\leq1$, $0\leq x''\leq1$, $0<y\leq1$, $0\leq y'\leq1$, $0\leq y''\leq1$, $x+x'+x''=1$ et $y+y'+y''=1$, et z est un nombre qui neutralise la charge du composé.

10. Dispositif électrochimique selon la revendication 9, dans lequel l'oxyde conducteur mixte à plusieurs composants est choisi dans l'ensemble constitué de la cobaltite de strontium et de lanthane, de la ferrite de cobalt, de strontium et de lanthane, de la cobaltite de baryum et de lanthane, de la ferrite de cobalt, de baryum et de lanthane et de la ferrite de cobalt et de strontium.

11. Dispositif électrochimique selon la revendication 1, dans lequel la couche d'anode et la couche de cathode de chaque cellule électrolytique plane respective comportent indépendamment un métal ou un alliage.

12. Dispositif électrochimique selon la revendication 11, dans lequel la couche d'anode et la couche de cathode de chaque cellule électrolytique plane respective contiennent de l'argent.

13. Dispositif électrochimique selon la revendication 1, dans lequel la couche d'interconnexion électriquement conductrice comporte un métal ou un alliage résistant à l'oxydation.

14. Dispositif électrochimique selon la revendication 1, dans lequel la couche d'interconnexion électriquement conductrice de chaque cellule électrolytique plane respective comporte un oxyde métallique électroniquement conducteur à plusieurs composants.

15. Dispositif électrochimique selon la revendication 14, dans lequel l'oxyde métallique électroniquement conducteur à plusieurs composants est choisi dans l'ensemble constitué de la manganite de strontium et de lanthane, de la chromite de strontium et de lanthane, de la manganite de calcium et de lanthane et de la chromite de calcium et de lanthane.

16. Dispositif électrochimique selon la revendication 2, dans lequel le moyen d'étanchéité maintient une étanchéité au gaz à des températures supérieures à 500° C et présente un coefficient de dilatation thermique comparable à celui de la couche d'interconnexion électriquement conductrice et de la couche d'électrolyte ioniquement conducteur.

17. Dispositif électrochimique selon la revendication 7, dans lequel le moyen d'étanchéité est choisi dans l'ensemble constitué du verre dévitrifié, du verre, des composites de verre et de céramique, des composites de verre et de métal, et des alliages et brasures métalliques résistant à l'oxydation.

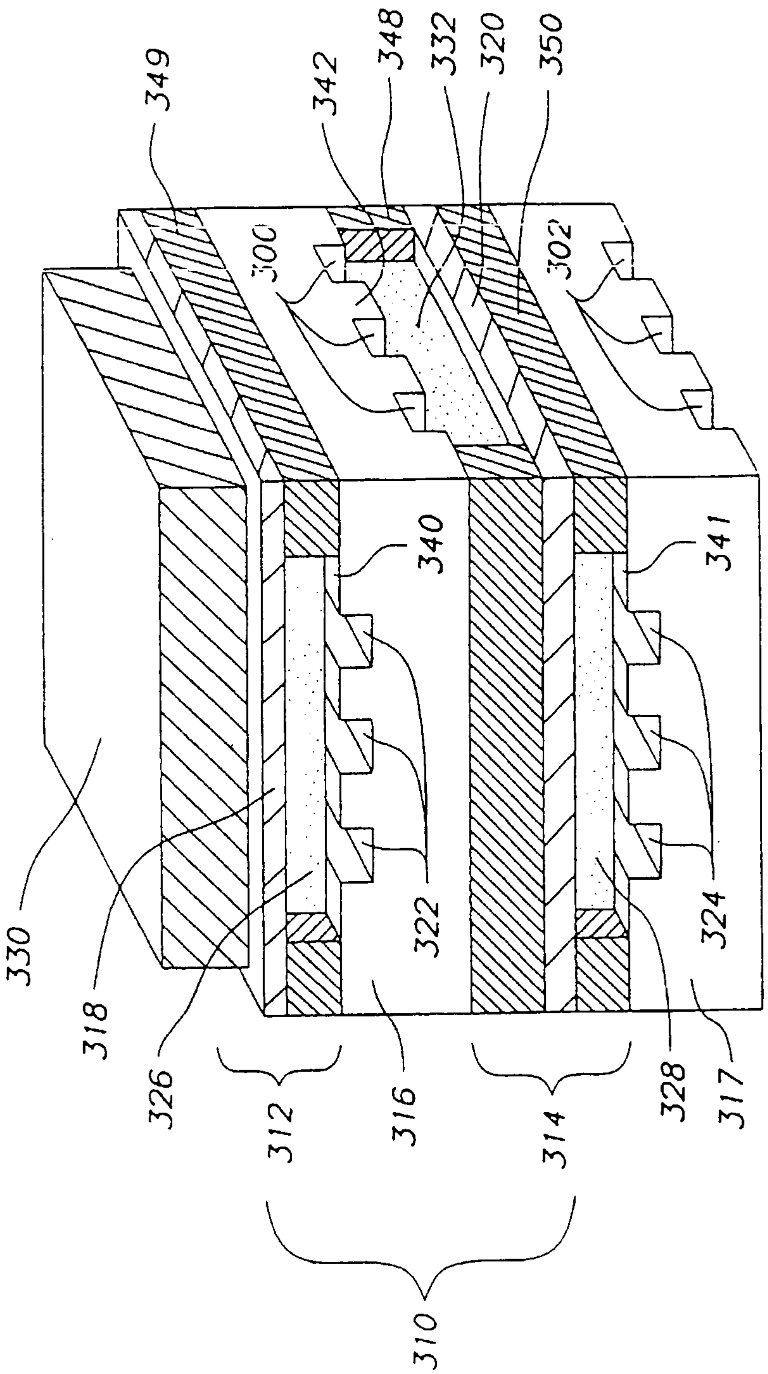
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FIG. 1

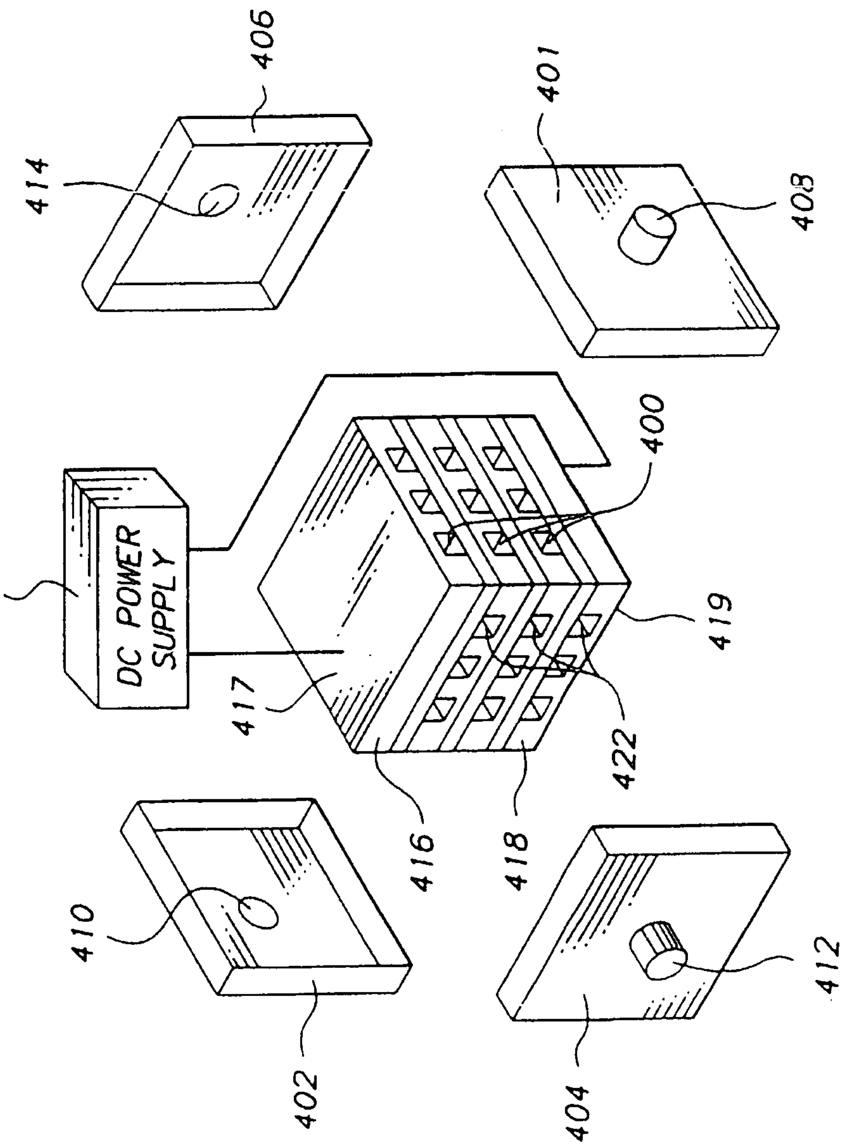
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FIG. 2

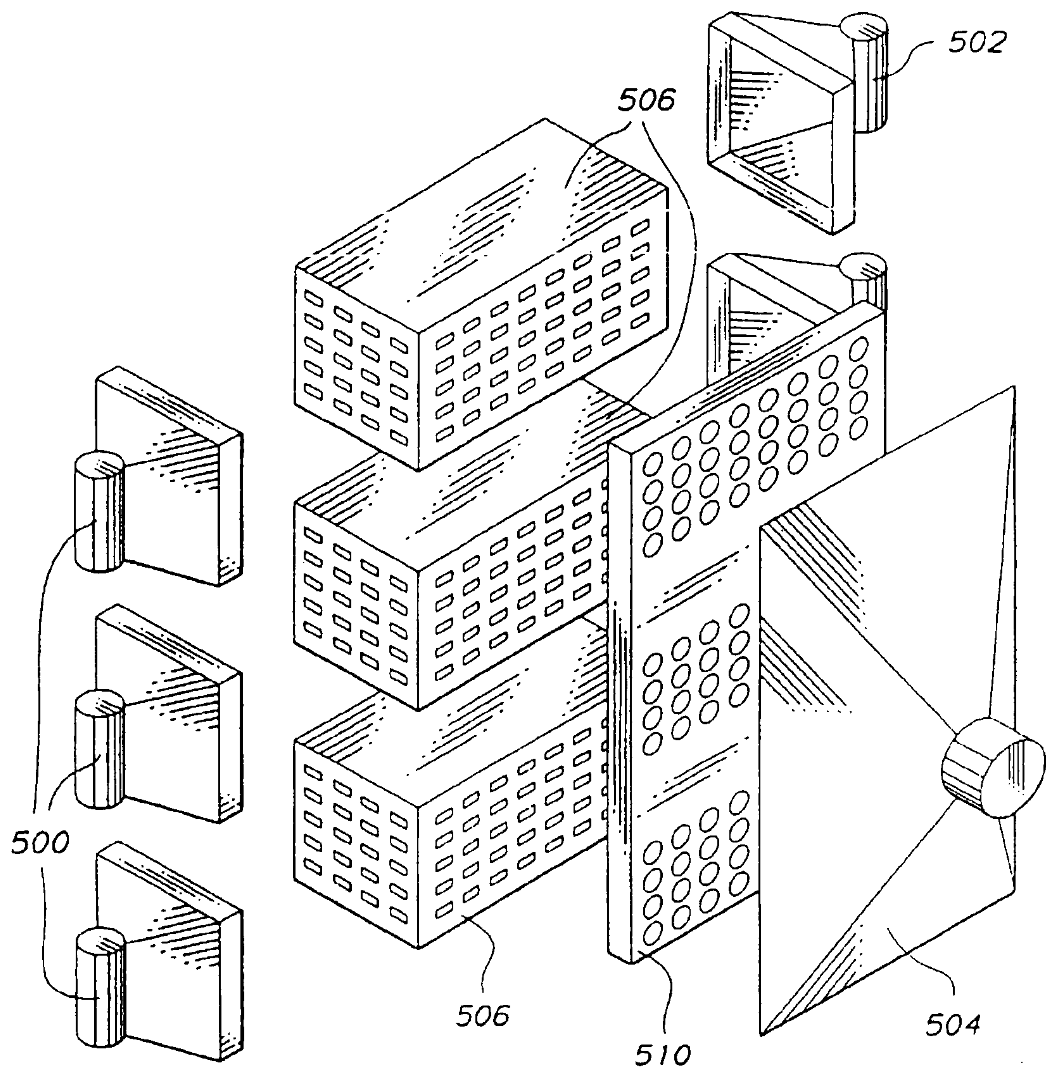

FIG. 3